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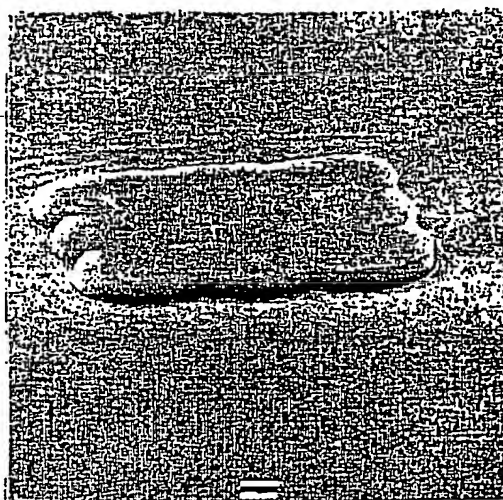
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(54) Title: **ELECTRON-BEAM CURING AND PATTERNING OF SOL-GEL**



(57) Abstract: A method for rapidly forming and developing a pattern having microscopic and/or nanoscopic features is provided. The method involves depositing a layer of a sol-gel composition on a surface of a substrate to form a sol-gel film, directing an electron beam at selected areas of the film to cure the selected areas of the film, and contacting the sol-gel film with a solvent to dissolve and remove areas of the film that have not been cured to leave a desired pattern of cured sol-gel material. The method is useful for rapid fabrication of miniature devices such as planar optical devices, photonic crystal waveguide structures, medical sensor and diagnostic devices, and for forming micro-molding or nano-molding tools that are useful for fabricating miniature optical, electronic, mechanical, medical, and other devices.

WO 02/17347 A1

## **ELECTRON-BEAM CURING AND PATTERNING OF SOL-GEL**

### **BACKGROUND OF THE INVENTION**

#### **5     1. Field of the Invention**

The present invention relates to the field of patterning a material deposited on a substrate, and more particularly to a method for creating patterns with ultra-fine features in a thin film carried on a surface of a substrate for uses such as fabricating as micro-molding or nano-molding tools or molds or photonic crystal structures.

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#### **2. Technical Background**

There are currently many competing technologies and materials that are used or are being studied for use in the fabrication of miniature devices having ultra-fine features such as microscopic or nanoscopic trenches, ridges, pillars, mesas, etc.

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Examples of devices having microscopic and/or nanoscopic features include planar optical devices or waveguides used in optical communications systems, semiconductor integrated electrical circuits, hybrid opto-electrical devices, as well as certain micro-mechanical or microelectro-mechanical systems (MEMS) devices, medical diagnostic devices, and so forth.

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Devices having microscopic and/or nanoscopic features are typically prepared using photolithographic techniques. First, a photo-mask is prepared having areas that are transparent to at least a particular radiation (e.g., ultraviolet radiation) which are surrounded by adjacent areas that are opaque to the particular radiation. The mask defines a pattern that is a replica of the desired pattern that is to be formed in a material at the surface of a substrate. Once an appropriate mask has been prepared, a desired relief pattern can be created in a substrate or in a film deposited on the surface of a

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substrate using conventional photolithography. Typically, a film (i.e., a thin layer of material) is deposited on a substrate using any of a variety of deposition or coating techniques, (e.g., sputtering, flame hydrolysis deposition, chemical vapor deposition, etc.). A photoresist layer (typically a polymer material) is deposited (such as by spin-coating) over the substrate or film layer that is to be patterned. Next, the photo-mask is positioned over the photoresist layer and radiation is directed at the mask and through the transparent areas of the mask to the photoresist layer. The areas of the photoresist layer that have been exposed to the radiation are chemically modified so that either the irradiated areas are soluble in a developer solvent (positive resist) or the non-irradiated areas are soluble in a developer solvent (negative resist), while the adjacent areas are insoluble in the developer solvent. After contacting the photoresist material with a developer solvent, a patterned resist layer that corresponds to a desired pattern for the substrate or film layer remains. Chemical etching or reactive ion etching may then be used to replicate the pattern into the substrate or film. Typical film materials include dielectric materials such as silica, semiconductive materials such as germanium-doped silica, and conductive materials such as copper, silver, gold, etc. These photolithographic techniques may be employed to form additional layers of patterned material to fabricate relatively complex devices having ultra-fine features. Although these techniques involving deposition, lithography, and etching are commonly employed for mass production of various devices, they have the disadvantages of being relatively expensive and are not ideally suited for rapid prototyping of devices.

An alternative process for patterning a substrate or a film on a substrate involves the use of micro-molding techniques. First, a layer of a moldable material is deposited on a surface of a substrate, or a film deposited on a substrate. The moldable material is a thermoplastic polymer that is heated to a temperature to allow sufficient softening to facilitate shaping of the moldable material during a compressive molding step. A molding tool having protruding features and adjacent recessed features is pressed into the moldable material so that the thickness of the moldable material under the protruding features is thinner than the thickness of the moldable material under the recessed features. A relief pattern corresponding to the features that are desired is thus created in the moldable material. The relief pattern generally conforms to the shape of the features of the molding tool. The molding tool is then removed from the moldable

material, and the molded material is processed such as by wet etching of reactive ion etching so that the thinner areas of the molded material in the relief are removed to expose the underlying substrate or film. Thus, the pattern in the molding tool is replicated in the moldable material. Thereafter, the pattern in the moldable material can be replicated in a material that is added onto the substrate. This can be achieved by depositing a material over the patterned moldable material and over the areas of the substrate film that have been exposed. Materials which may be deposited on the exposed areas of the substrate film include electrical conductors, semiconductors, ceramics, glasses, or dielectrics of the type commonly used to fabricate integrated electrical circuits, optical circuits, etc. Next, a lift off technique is performed in which a selective chemical etch is applied to remove the remaining moldable material and any material deposited on the moldable material, leaving a replica of the pattern in the material deposited on the substrate film. Alternatively, the pattern in the moldable material can be replicated directly into the substrate or a film deposited on the substrate using an etching process such as ion etching or chemical etching, such that recesses are formed in the areas of the substrate or film deposited on the substrate that are exposed through the molded and patterned thermoplastic layer.

These micro-molding techniques may be advantageously employed to mass-produce devices having ultra-fine features at a low cost. However, there are certain disadvantages associated with the micro-molding tools used in these processes. A first disadvantage relates to the process by which the micro-molding tools are prepared. Typically, a micro-molding tool is prepared using the conventional lithographic techniques that are to a certain extent avoided when the micro-molding tools are employed to fabricate devices. In order to facilitate mass production, and to replace damaged or worn micro-molding tools, a relatively large number of micro-molding tools may need to be fabricated. Typically, each of these micro-molding tools is separately prepared from a hard substrate such as a metal, glass or ceramic material by depositing a photoresist layer on the substrate, exposing the photoresist material to radiation through a mask, developing the desired pattern in the photoresist material, and etching the substrate. Thus, preparation of the micro-molding tools can be expensive and time consuming. Another problem associated with micro-molding tools fabricated of materials such as metals, glasses or ceramics is that the thermoplastic materials that

are patterned with the micro-molding tools can tend to stick to the surfaces of the micro-molding tools which can cause pattern defects. A release agent may be used to facilitate smoother release of the patterned material from the micro-molding tools whereby pattern defects can be eliminated or reduced, however; mold release agents wear off the mold surfaces and must be regularly reapplied. Regular application of a mold release agent on surfaces of a micro-molding tool requires additional labor and equipment. Another problem with release agents is that they may adversely affect properties (i.e., functionality) of the devices being fabricated or subsequent steps during fabrication. For example, release agents can interfere with subsequent fabrication steps involving the use of adhesives (i.e., release agents can prevent adhesives from effectively adhering to surfaces). While such problems can be overcome, they add to the cost and complexity of the process.

In view of the known processes for creating a pattern having ultra-fine features in a substrate or in a film of material on a substrate, there exists a need for improved processes that are efficient and less expensive. Further, there is a need for micro-molding tools having a functional surface such as a highly non-wetting surface that eliminates the need for release agents on such micro-molding tool surfaces.

#### SUMMARY OF THE INVENTION

This invention concerns a process for creating a pattern with ultra-fine features on a surface of a substrate or in a film deposited on a surface of a substrate.

The method of the present invention may be advantageously used for directly patterning a material on the surface of a substrate for the fabrication of various miniature devices such as planar optical devices or waveguides, semiconductor integrated electrical devices, opto-electrical devices, and so forth, without employing conventional lithographic and etching techniques.

The method of this invention may also be advantageously used for fabricating micro-molding tools that can be employed in the mass production of miniature devices having a patterned material with microscopic and/or nanoscopic features. More particularly, the invention facilitates rapid fabrication of inexpensive prototypes and/or micro-molding tools.

The method of this invention may also be used to fabricate integrated optical or "planar" type photonic crystal waveguide structures.

In accordance with an aspect of this invention, a process for solidifying (or "curing") and patterning a sol-gel composition on a substrate is provided. The process involves depositing a layer of a sol-gel composition on a surface of a substrate to form a sol-gel film, curing or solidifying selected areas of the film that correspond to a predetermined desired pattern by directing an electron-beam at those selected areas of the sol-gel film, and contacting the partially cured sol-gel with a solvent to dissolve and remove areas of the sol-gel film that have not been cured to leave the predetermined pattern of cured sol-gel material.

The process also allows direct patterning and curing of a sol-gel film to create ultra-fine features. The desired pattern is created in a solid glass-like material without conventional lithography techniques, (e.g., radiation exposure through a mask and development), and without convention etching techniques.

Additional features and advantages of the invention will be set forth in the detailed description which follows and will be apparent to those skilled in the art from the description or recognized by practicing the invention as described in the description which follows together with the claims and appended drawings.

It is to be understood that the foregoing description is exemplary of the invention only and is intended to provide an overview for the understanding of the nature and character of the invention as it is defined by the claims. The accompanying drawings are included to provide a further understanding of the invention and are incorporated and constitute part of this specification. The drawings illustrate various features and embodiments of the invention which, together with their description serve to explain the principals and operation of the invention.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1-7 are scanning electron micrographs (SEMs) of a patterned sol-gel film prepared using a process of the invention;

Figures 8-11 are SEMs of photonic crystal waveguide structures fabricated using sol-gel photomasks fabricated using the method of the present invention as described herein; and

Figures 12-17 are SEMs of sol-gel photomasks fabricated using the process of the present invention as described.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 The present invention utilizes the discovery that a sol-gel film may be cured (solidified) by directing an electron beam at the sol-gel film, and that electron-beam curing of the sol-gel film can be used for creating a patterned glass-like material having ultra-fine features.

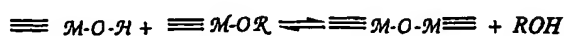
10 In particular, a desired pattern having ultra-fine features (for example, such as those normally associated with conventional photonic crystal waveguide structures, or micro-molding and nano-molding tools or molds) can be directly written into a sol-gel film using an electron beam. Ultra-fine features are features having dimensions in the microscopic range and/or the nanoscopic range (e.g., dimensions from about 100 nanometers or less up to about 1,000 micrometers or more), with a resolution (i.e.,  
15 variation from a desired dimension) that is less than or about 5 nanometers.

The process for curing and patterning a sol-gel composition on a surface of a substrate in accordance with the principles of this invention involves first depositing a sol-gel composition onto a substrate to form a thin layer or film. Sol-gel compositions are well known. Such compositions are comprised of at least one compound that can  
20 be hydrolyzed and condensed to form a metal oxide or metalloid oxide structure in which a metal atom or a metalloid atom is connected with a plurality of other metal or metalloid atoms through bridging oxygen atoms. The hydrolyzable/condensable compound or compounds present in a sol-gel are compounds that are capable of being thermally cured through a series of hydrolysis reactions, alcohol condensation  
25 reactions, and water condensation reactions in accordance with the following general reaction sequence.

(Hydrolysis)

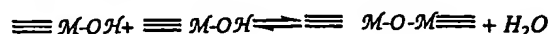


(Alcohol condensation)



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(Water condensation)



The above reaction scheme trivializes, but also facilitates understanding of, the complex processes of hydrolysis and polycondensation that produce the fully cured, or at least substantially fully cured products. The hydrolyzable/condensable compounds in the sol-gel composition can be represented by the general formula  $M(OR)_nX_m$ , where  $M$  is a metal or metalloid (e.g., an electrically semiconductive material) having a valence of  $n + m$ , each  $R$  is independently a hydrogen or a hydrocarbyl group (e.g., an alkyl group) each  $X$  is an organic group that does not participate in the hydrolysis or condensation reactions,  $n$  is a positive integer,  $m$  is zero or a positive integer, and  $n + m$  is equal to the valence of the metal or metalloid atom,  $M$ . Examples of metal or metalloid atoms,  $M$ , that may be used include *Si, Ti, Al, Ge, Ta, B, Ga, Zr* and *Sb*. In order to provide a highly cross-linked condensed metal oxide or metalloid network having properties comparable to that of glass, it is desirable that a high proportion of the hydrolyzable/condensable compounds in the sol-gel composition are fully hydrolyzable, i.e., are represented by the general formula  $M(OR)_n$ , where  $M, R$ , and  $n$  are defined above. Examples of such compounds include tetraethylorthosilicate (TEOS) and tetrakisopropoxygermane (TIPG). The sol-gel compositions may contain relatively minor amounts of partially hydrolyzable/condensable compounds having the general formula  $M(OR)_nX_m$ , where  $M, R, X$ , and  $n$  are as defined above, and  $m$  is a positive integer. An example of a compound of this type is methacryloxypropyltrimethoxysilane (MPTS). Partially hydrolyzable compounds having an organic group (e.g., MPTS) may be employed in the sol-gel composition to impart greater flexibility to the cured or condensed solid metal oxide or metalloid oxide network derived from the sol-gel composition. Cured materials prepared from sol-gel compositions containing partially hydrolyzable compounds having an organic group that does not participate in the hydrolysis or condensation reactions may also exhibit enhanced toughness, reduced brittleness, and relatively thicker films (up to 10 nanometers or more) may be cured without cracking using the electron-beam patterning and curing technique of this invention.

The sol-gel cladding compositions of this invention may also contain a partially hydrolyzable fluorine-containing compound in an amount that is effective to provide a highly non-wetting surface that eliminates, or substantially reduces, the need for release



agents on surfaces of the patterned material, when the patterned material is used on a micro-molding tool. The partially hydrolyzable fluorine-containing compounds include a metal atom or metalloid atom, such as *Si, Ti, Al, Ge, Ta, B, Ga, Zr* or *Sb*, at least one hydrolyzable group (e.g., an alkoxy group) and at least one non-hydrolyzable group that contains at least one fluorine atom. Examples of partially hydrolyzable fluorine-containing compounds suitable for use in the sol-gel compositions utilized in the processes of this invention may be represented by the general formula  $M(OR)_pZ_q$ , where *M* is a metal or metalloid atom having a valence of  $p + q$ , each *R* is independently a hydrogen atom or a hydrocarbyl group (e.g., an alkyl group), each *Z* is a fluorine-containing group, and *p* and *q* are each at least 1. The fluorine-containing group may be an alkyl group having fluorine substituents, and partially hydrolyzable fluorine-containing compounds include fluoroalkyltrialkoxysilanes, such as (3,3,3-trifluoropropyl) trimethoxysilane. The amount of partially hydrolyzable fluorine-containing compound that may be required to achieve a desired non-wetting surface can be determined by routine experimentation. An example of a sol-gel composition containing a partially hydrolyzable fluorine-containing compound in an amount sufficient to impart a non-wetting surface (hydrophobic surface) to a cured material derived from the composition is set forth below. Partially hydrolyzable fluorine-containing compounds may also be added to sol-gel compositions in order to lower the refractive index of a cured material derived from the composition. Thus, partially hydrolyzable fluorine-containing compounds may be utilized in those situations in which a micro-molding tool is prepared with a release surface, and in those situations in which optical devices having components with a low refractive index are fabricated.

The sol-gel composition of this invention can contain other ingredients. For example, partially hydrolyzable compounds having a non-hydrolyzable moiety that is organically polymerizable may be added, either with or without other non-hydrolyzable, organically polymerizable compounds (e.g., polymerizable ethylenically unsaturated monomers such as methacrylic acid or a methacrylic acid ester). However, sol-gel compositions containing a high proportion of fully hydrolyzable compounds, and a relatively low proportion of partially hydrolyzable compounds and non-hydrolyzable compounds, are suitable. Such compositions, when thermally cured, will have properties similar to glass, whereas compositions containing a relatively high

proportion of partially hydrolyzable, organically functionalized compounds and non-hydrolyzable, organic monomers, will tend to exhibit hybrid properties intermediate between that of an organic polymer and a glass material. Sol-gel compositions for use in the processes of this invention may have a mole ratio of fully hydrolyzable

5 compounds (compound in which each of the moieties bonded to a metal or metalloid atom are capable of being hydrolyzed so that an alkoxy group bonded to the metal or metalloid atom is replaced with a hydroxyl group) to partially hydrolyzable compounds (compounds that include at least one moiety that is not capable of being hydrolyzed) is at least 50:50 and more suitably at least 70:30. The compositions should contain little,  
10 if any, organic monomers.

The sol-gel compositions of this invention may be deposited on the surface of a substrate using any suitable coating technique, such as spin-coating or dip-coating. Suitable coating thicknesses depend on the particular application for the device or micro-molding tool being fabricated using the processes of the invention. However,  
15 typical sol-gel film thicknesses are from about 1 or 2 micrometers to about 10 or 15 micrometers.

After the sol-gel composition has been deposited to form a film, the film may be prebaked to partially cure the sol-gel composition to stabilize the film on the substrate, and/or to eliminate tackiness at the surface of the substrate. However, a preheating step  
20 is not required, and may not be desirable in many applications.

A desired pattern can be formed in the sol-gel film by selectively curing predetermined areas of the sol-gel film that correspond to a desired pattern by directing an electron beam at the selected areas of the film. In other words, a desired pattern is written directly into the sol-gel film using an electron beam. An apparatus for  
25 patterning and curing a sol-gel film by writing the desired pattern directly into the sol-gel film using an electron beam can be provide by converting a scanning electron microscope (e.g., JEOL 840) for use as an electron beam patterning tool using a commercially available SEM conversion package. The commercially available package includes pattern generation software and hardware that directs the electron  
30 beam to write patterns that are created by the user in a computer aided design (CAD) software package. A system of this type is capable of writing generally any type of pattern that can be drawn using the CAD software.

Although the mechanism by which curing of the sol-gel film is achieved using an electron beam is perhaps not fully understood, it is believed that the electron beam induces localized heating of the sol-gel film, and that this localized heating causes localized curing or condensation of the sol-film in those areas of the film bombarded with or exposed to the electron beam by way of the hydrolysis and condensation reactions schematically illustrated above. The cured areas of the sol-gel film form a condensed three-dimensional network comprised of metal or metalloid atoms linked together through an oxygen atom. The resulting cured product has chemical and physical properties that are very similar, and in some cases almost identical, to conventional glasses.

After the desired pattern has been written into sol-gel film, the film is contacted with a solvent to dissolve areas of the film that have not been cured. This allows the uncured areas of the film to be easily removed, leaving behind the desired pattern of cured sol-gel material. A suitable solvent that may be used to remove the areas of the sol-gel film that have not been cured is toluene. In order to improve the wettability and effectiveness of the solvent, the solvent may include a small amount of a surfactant.

The processes of this invention may be used to fabricate optical waveguides for planar optical devices, microfluidic channels for biological sensing devices and/or biological diagnostic devices, etc. Alternatively, the processes of this invention may be used to design patterns for micro-molding tools that may be used during the fabrication of various miniature devices including planar optical devices, semiconductor electrical circuit devices, etc.

#### Examples

The following examples further illustrate certain concepts and embodiments of the invention, and do not limit the scope of the invention.

Electron-beam patterning of sol-gel films was accomplished by using a custom built electron-beam lithography system. The system was based on a JEOL 840 scanning electron microscope that was converted to write patterns using a commercially available SEM conversion package. The package included pattern generation software and hardware that is used to direct the electron beam to write

patterns that are created by the user in a computer aided design (CAD) software package.

5 Figs. 1-7 show scanning electron microscope images of test pattern wheels written using electron-beam lithography into an inorganic-organic hybrid sol-gel material in accordance with the principles of this invention.

Fig. 1 is an overall view of a 3 X 3 pattern of wheels and Figs. 2-7 are magnified images of individual wheels. The wheel patterns shown in Figs. 3-5 were written at electron-beam dosages of 90, 150, and 270 nC/cm respectively. The sol-gel composition used in these experiments was comprised of 53.6 mole percent of  
10 tetraethylorthosilicate (TEOS), 13.4 mole percent tetraisopropoxygermane (TIPG), and 33 mole percent methacryloxypropyltrimethoxysilane (MPTS). The composition is UV sensitive on account of the methacryloxy group on the MPTS, and can be patterned with light at 248 nm which cross links double bonds on the MPTS. The sol-gel composition was deposited onto a substrate using a spin-coating technique to provide a  
15 sol-gel film having a uniform thickness of from about 0.5 to 6 microns. When the sol-gel films were exposed to an electron beam and developed (contacted with a solvent such as toluene to dissolve and remove the area of the film that have not been exposed to, or written with, the electron beam), the film behaved as a negative resist. Infrared spectra of the electron-beam cured film did not show any decrease in the band  
20 corresponding to the double bond of MPTS. When the same films were cured by exposure to ultraviolet radiation, infrared spectra indicated that the double bond disappeared. This demonstrates the curing mechanism for electron-beam curing is not by cross-linking of the double bond. In fact, the infrared spectra showed that essentially none of the double bonds in the MPTS were reacted after exposure to an  
25 electron beam. An expanded FTIR spectra showed that OH stretch as a function of electron-beam dosage decreased with increasing electron-beam energy. This is consistent with a conventional sol-gel condensation reaction in which a silica framework is formed. It is believed that the electron beam catalyzes the condensation step described above to form a silica glass framework.

30 In the examples illustrated in Figs. 1-7, films having a thickness of from 0.5 to 6 microns were used to write lines having a width of about 100 nanometers. Fig. 1 shows a mesa-like structure having the 3 X 3 wheel pattern written on the top surface of the

mesa-like structure. It is believed that electron scattering coupled with thermal conduction cured the surrounding areas of the wheels. The magnified images shown in Figs. 2-7 show very well defined wheel patterns (a circular rim with spokes extending radially from the center of the wheel to the rim). This is due to the focus or  
5 concentration of the electron beam on the surface of the sol-gel film. Two unique results are obtained. First, the linewidths of the wheels are about 100 nanometers, and provide positive relief on top of the mesa-like structure. This structure can be used as a nanoimprint mold (i.e., a nano-molding tool) to emboss only the wheel lines into a thin polymer film. The second result is that the areas of the mesa-like structure that were  
10 not directly written upon with the electron beam (i.e., the areas between the spokes and rim, and the areas outside of the rim that are immediately adjacent the rim) formed a relatively large structure. Thus, the processes of the invention have utility in rapidly writing large structures (e.g., long waveguides), and may allow direct fabrication of micromolds with tailored surface properties. For example, a pure TEOS sol-gel film  
15 may be patterned with an electron beam to rapidly form a waveguide having properties that are substantially the same as a glass waveguide formed using more conventional methods such as flame hydrolysis deposition or chemical vapor deposition.

Referring particularly to Figs. 8-17, photonic crystal waveguide structures fabricated using the electron-beam cured sol-gel photomask technique according to the  
20 present invention are shown in Figs. 8-11, and the sol-gel photomasks utilized to prepare photonic crystal structures are shown in Figs. 12-17. It may be seen that each fabrication process can produce photomasks and waveguide paths having a lattice or array of holes (or "wells") and wall structures disposed on opposing sides of the waveguide, with the side walls of the holes and walls evidencing good depth, side wall  
25 smoothness, and verticality. The examples shown in Figs. 8-11 depict photonic crystals having generally circular holes, whereas Figs. 12-15 depict photomasks having a more rectangular configuration of substantially similar pitch (hole-to-hole center spacing) and thin wall thickness. It may be appreciated that a wide variety of suitable photonic crystal waveguide structures of the desired shape, pitch, wall thickness, and array or  
30 lattice structure may be fabricated using the process of the present invention, and used to achieve any number of photonic crystal device or waveguide patterns, such as the right-angle bends shown in Figs. 8-15, X- and Y-splits for couplers or switches as

shown in Figures 16 and 17, or any other pattern or array that might be suitable and appropriate to accomplish desired light-guiding properties. It may also be readily appreciated that the method of the present invention may be utilized to fabricate other types of photonic crystal structures, such as a waveguide having an array of rods (rather than holes or wells) disposed on opposing sides of the waveguide, and other patterns conventionally utilized in fashioning photonic crystal structures. It is also understood that the method of the present invention may lead to the fabrication of new and unique photonic crystal waveguide structures and patterns (particularly considering multi-layer or three-dimensional photonic crystal structures or waveguide patterns otherwise requiring repeated or overlapping lithographic and etching steps) that would be impracticable or impossible to achieve using conventional patterning and etching processes with silica-on-insulator materials.

Further background information relevant to sol-gel compositions, the formation of sol-gel films, methods for patterning, curing, and etching of such sol-gels, and the fabrication of waveguides and other structures using sol-gels are contained in United States Patent Applications Serial Nos. 09/319,800 (filed December 12, 1997) and 09/494,073 (filed January 28, 2000), as well as the United States Patent Application of Hancock, Ukrainczuk, and Sewalt filed on August 17, 2000 entitled Direct Writing of Waveguides in Sol-Gels [Serial No. not yet assigned], which are each incorporated herein by reference as though fully set forth.

It will become apparent to those skilled in the art that various modifications to the preferred embodiment of the invention as described herein can be made without departing from the spirit or scope of the invention as defined by the appended claims.

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What is claimed is:

1. A method for solidifying and patterning a sol-gel composition on a surface of a substrate to form a predetermined pattern of cured sol-gel material, the method comprising the steps of:
  - 5 depositing a layer of the sol-gel composition on the surface of the substrate to form a sol-gel film;
  - directing an electron beam at selected areas of the sol-gel film to cure the selected areas of the sol-gel film; and
  - 10 contacting the sol-gel film with a solvent to remove areas of the sol-gel film that have not been cured, leaving the selected areas of the sol-gel film corresponding to the predetermined pattern of cured sol-gel material.
2. The method of claim 1 wherein the sol-gel composition includes at least one fully hydrolyzable compound having the general formula  $M(OR)_n$ , where  $M$  is a metal atom or a metalloid atom having a valence of  $n$ , and each  $R$  is independently a hydrogen or hydrocarbyl group.
3. The method of claim 2 wherein each  $R$  is independently an alkyl group.
4. The method of claim 3 wherein the metal atom or the metalloid atom,  $M$ , is selected from the group consisting of Si, Ti, Al, Ge, Ta, B, Ga, Zr, and Sb.
5. The method of claim 2 wherein the sol-gel composition further includes a partially hydrolyzable fluorine-containing compound.
6. The method of claim 5 wherein the partially hydrolyzable fluorine-containing compound is represented by the general formula  $M'(OR')_p Z_q$ , where  $M'$  is a metal atom or a metalloid atom having a valence of  $p + q$ , each  $R'$  is independently a hydrogen or a hydrocarbyl group, each  $Z$  is a fluorine-containing group, and  $s$  and  $t$  are each at least 1.

7. The method of claim 6 wherein each  $R'$  group is independently an alkyl group, and each fluorine-containing group is an alkyl group having fluorine substituents.

5 8. The method of claim 7 wherein the partially hydrolyzable fluorine-containing compound is (3,3,3-trifluoropropyl) trimethoxysilane.

9. The method of claim 7 wherein the ratio of fully hydrolyzable compound to partially hydrolyzable fluorine-containing compound is at least 50:50.

10 10. The method of claim 7 wherein the ratio of fully hydrolyzable compound to partially hydrolyzable fluorine-containing compound is at least 70:30.

11. The method of claim 6 wherein the partially hydrolyzable fluorine-containing compound is present in an amount that is effective to impart a non-wetting,  
15 hydrophobic surface to the cured sol-gel material.

12. A method for making a micro-molding tool or a nano-molding tool having a predetermined pattern of protruding features adjacent recessed features, the micro-molding tool or a nano-molding tool being fabricated using a sol-gel composition on a  
20 substrate having a surface, the method comprising the steps of:

depositing a layer of the sol-gel composition on the surface of the substrate to form a sol-gel film;

directing an electron beam at selected areas of the sol-gel film to cure areas of the sol-gel film corresponding to the predetermined pattern of protruding features adjacent recessed features; and  
25

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contacting the film with a solvent to remove those areas of the sol-gel film that have not been cured, leaving the selected areas of the sol-gel film corresponding to the predetermined pattern of of protruding features adjacent recessed features forming the micro-molding tool or the nano-molding tool.  
30



13. The method of claim 12 wherein the sol-gel composition includes at least one fully hydrolyzable compound having the general formula  $M(OR)_n$ , where  $M$  is a metal atom or a metalloid atom having a valence of  $n$ , and each  $R$  is independently a hydrogen or hydrocarbyl group.

5

14. The method of claim 13 wherein each  $R$  is independently an alkyl group.

15. The method of claim 14 wherein the metal atom or the metalloid atom,  $M$ , is selected from the group consisting of Si, Ti, Al, Ge, Ta, B, Ga, Zr, and Sb.

10

16. The method of claim 13 wherein the sol-gel composition includes a partially hydrolyzable fluorine-containing compound.

15

17. The method of claim 16 wherein the partially hydrolyzable fluorine-containing compound is represented by the general formula  $M'(OR')_p Z_q$ , where  $M'$  is a metal atom or a metalloid atom having a valence of  $p + q$ , each  $R'$  is independently a hydrogen or a hydrocarbyl group, each  $Z$  is a fluorine-containing group, and  $s$  and  $t$  are each at least 1.

20

18. The method of claim 17 wherein each  $R'$  group is independently an alkyl group, and each fluorine-containing group is an alkyl group having fluorine substituents.

19. The method of claim 18 wherein the partially hydrolyzable fluorine-containing compound is (3,3,3-trifluoropropyl) trimethoxysilane.

25

20. The method of claim 18 wherein the ratio of fully hydrolyzable compound to partially hydrolyzable fluorine-containing compound is at least 50:50.

30

21. The method of claim 18 wherein the ratio of fully hydrolyzable compound to partially hydrolyzable fluorine-containing compound is at least 70:30.

22. The method of claim 17 wherein the partially hydrolyzable fluorine-containing compound is present in an amount that is effective to impart a non-wetting, hydrophobic surface to the cured sol-gel material.

5 23. A method for making a photonic crystal waveguide structure using a sol-gel composition on a substrate having a surface, the photonic crystal waveguide structure including a predetermined array of light-guiding structures, the method comprising the steps of:

10        depositing a layer of the sol-gel composition on the surface of the substrate to form a sol-gel film;  
      directing an electron beam at selected areas of the sol-gel film to cure areas of the sol-gel film corresponding to the predetermined array of light-guiding structures; and  
15        contacting the film with a solvent to remove those areas of the sol-gel film that have not been cured, leaving the selected areas of the sol-gel film corresponding to the predetermined array of light-guiding structures forming the photonic crystal waveguide structure.

20 24. The method of claim 23 wherein the sol-gel composition includes at least one fully hydrolyzable compound having the general formula  $M(OR)_n$ , where  $M$  is a metal atom or a metalloid atom having a valence of  $n$ , and each  $R$  is independently a hydrogen or hydrocarbyl group.

25 25. The method of claim 24 wherein each  $R$  is independently an alkyl group.

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26. The method of claim 24 wherein the metal atom or the metalloid atom,  $M$ , is selected from the group consisting of Si, Ti, Al, Ge, Ta, B, Ga, Zr, and Sb.

30 27. The method of claim 23 wherein the sol-gel composition includes a partially hydrolyzable fluorine-containing compound.

28. The method of claim 27 wherein the partially hydrolyzable fluorine-containing compound is represented by the general formula  $M'(OR')_p Z_q$ , where M is a metal atom or a metalloid atom having a valence of  $p + q$ , each  $R'$  is independently a hydrogen or a hydrocarbyl group, each Z is a fluorine-containing group, and  $s$  and  $t$  are each at least 1.

29. The method of claim 28 wherein each  $R'$  group is independently an alkyl group, and each fluorine-containing group is an alkyl group having fluorine substituents.

30. The method of claim 27 wherein the partially hydrolyzable fluorine-containing compound is (3,3,3-trifluoropropyl) trimethoxysilane.

31. The method of claim 27 wherein the ratio of fully hydrolyzable compound to partially hydrolyzable fluorine-containing compound is at least 50:50.

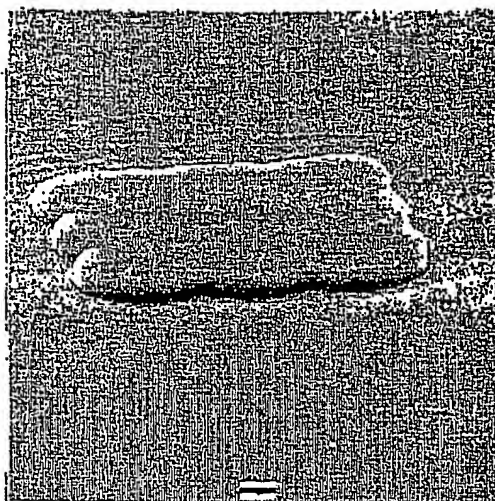
32. The method of claim 27 wherein the ratio of fully hydrolyzable compound to partially hydrolyzable fluorine-containing compound is at least 70:30.

33. The method of claim 27 wherein the partially hydrolyzable fluorine-containing compound is present in an amount that is effective to impart a non-wetting, hydrophobic surface to the cured sol-gel material.

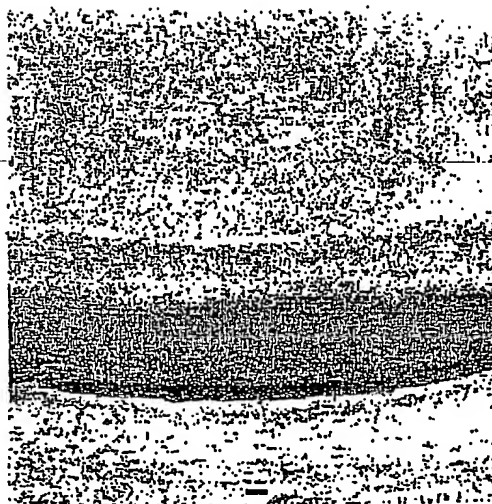
34. The method of claim 23 wherein the predetermined array of light-guiding structures includes a waveguide core and a plurality of holes formed proximate to the waveguide core.

35. The method of claim 34 wherein the waveguide core has opposing sides and the plurality of holes formed proximate to the waveguide core are disposed on the opposing sides of the waveguide core in a repeating pattern.

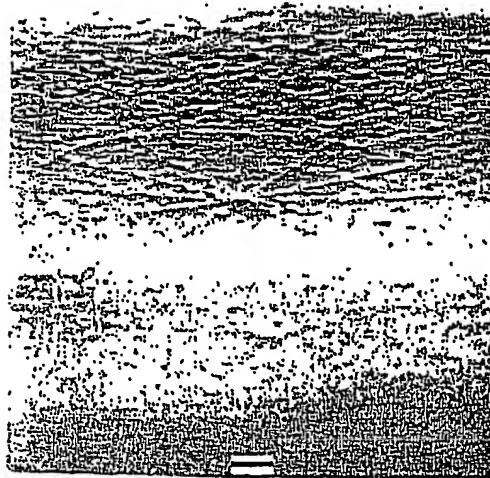
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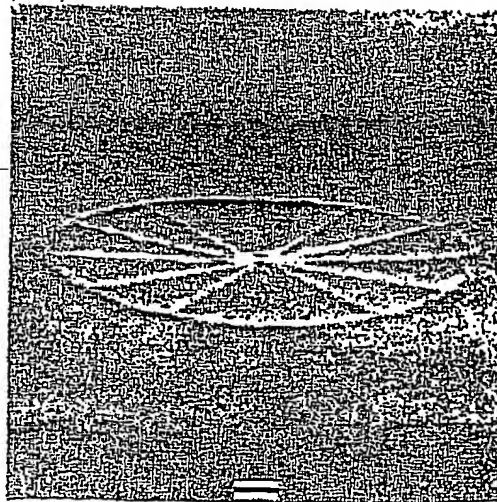
*Figure 1*



*Figure 2*



*Figure 3*

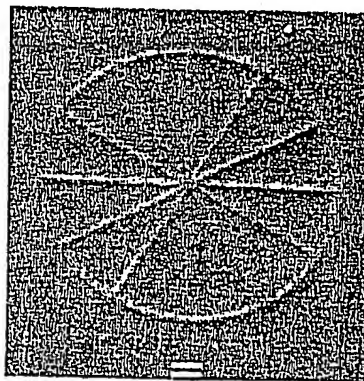


*Figure 4*

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*Figure 5*

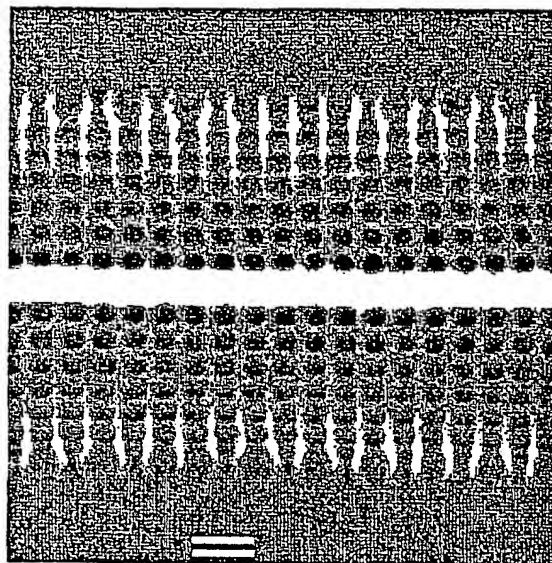


*Figure 6*



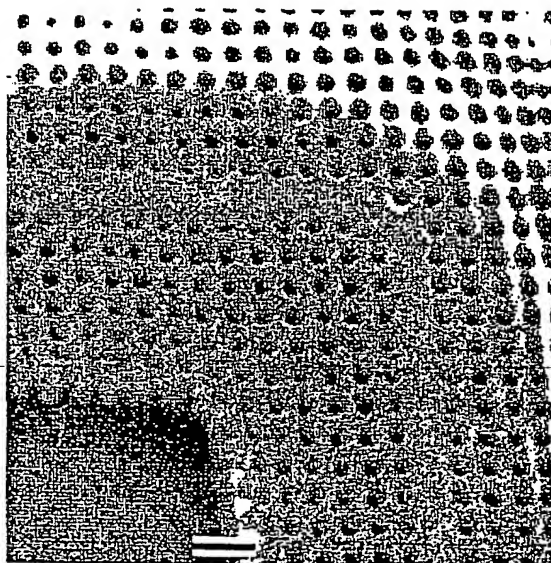
*Figure 7*

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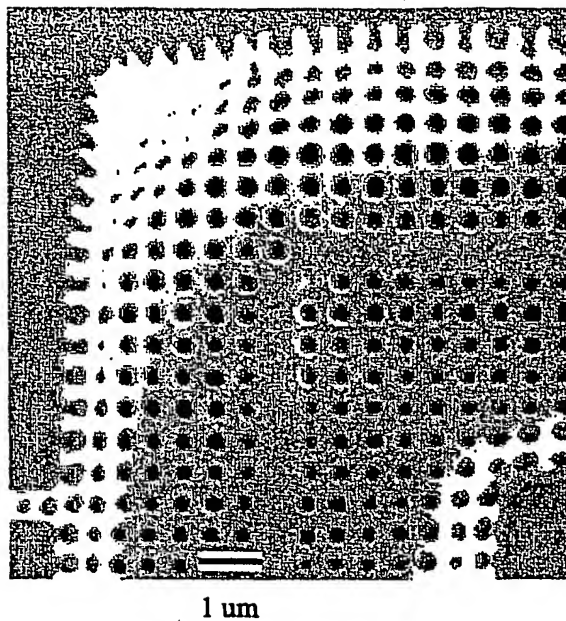
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*Figure 8*

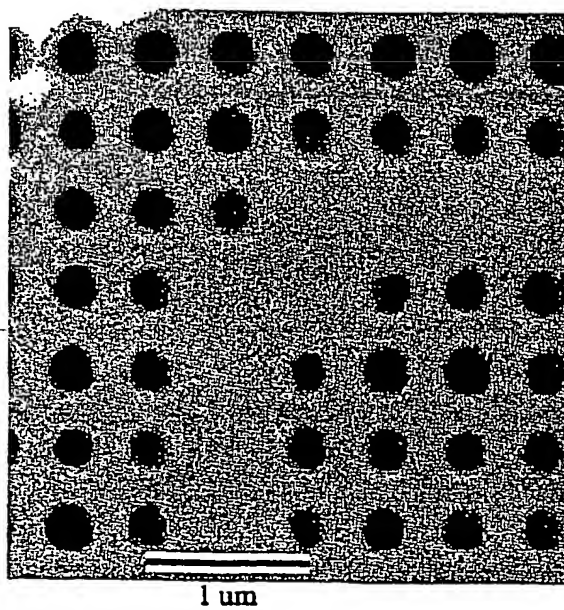


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*Figure 9*



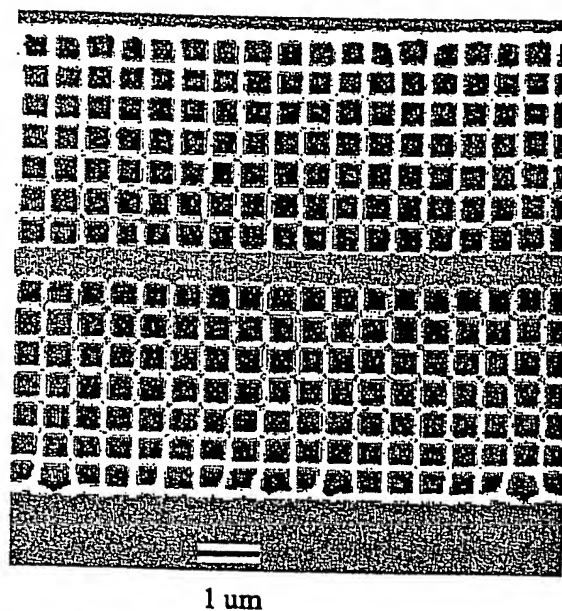
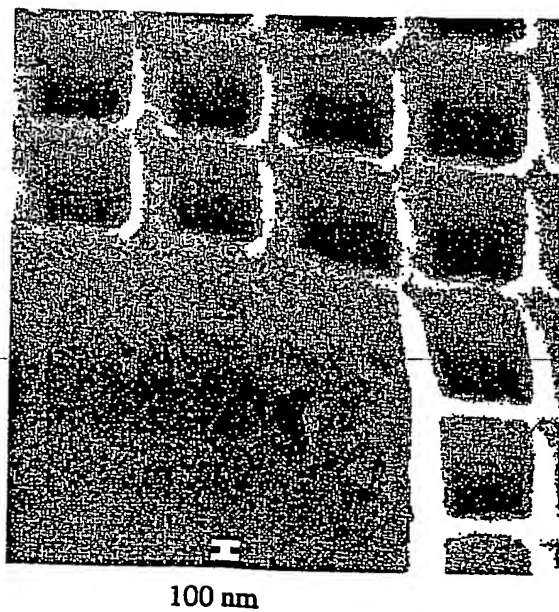
*Figure 10*



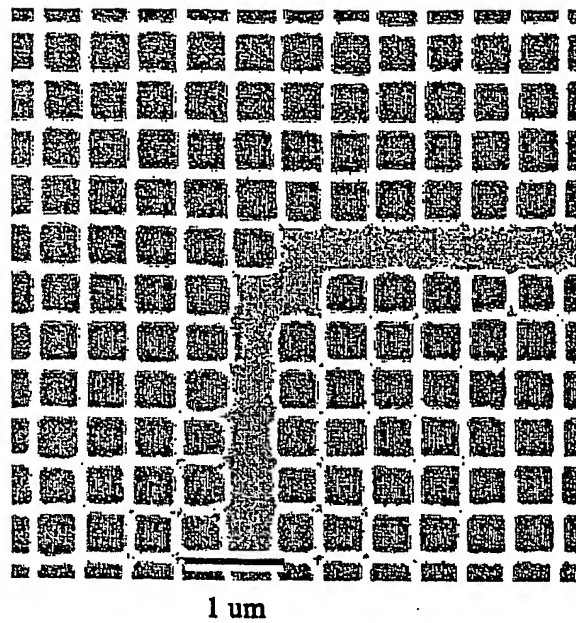
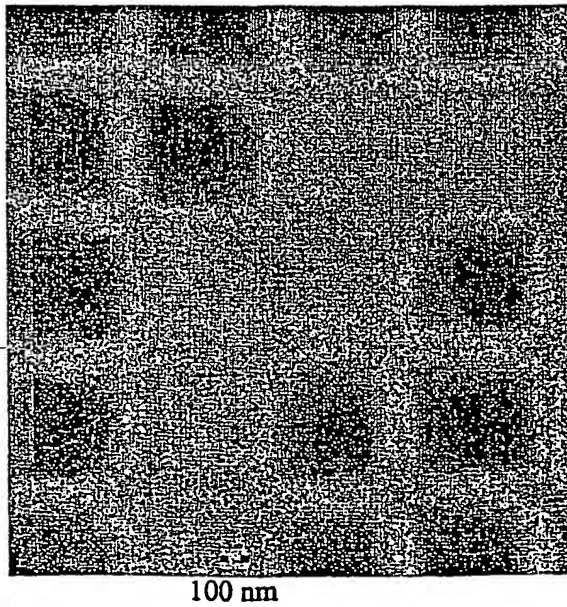
*Figure 11*



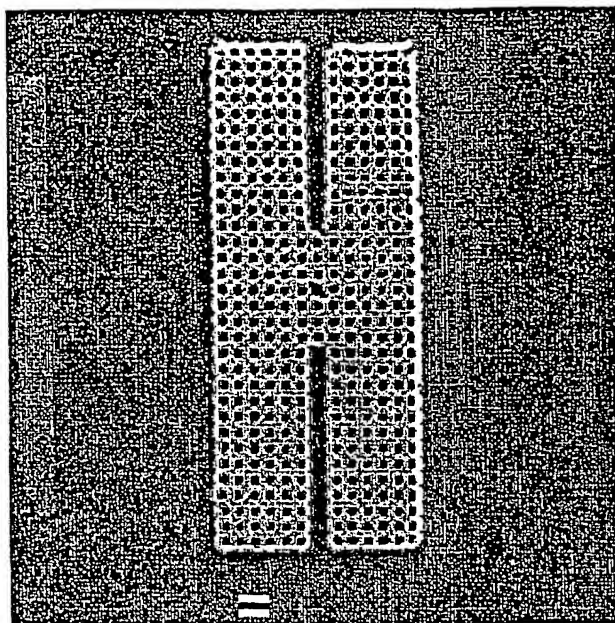
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*Figure 12**Figure 13*

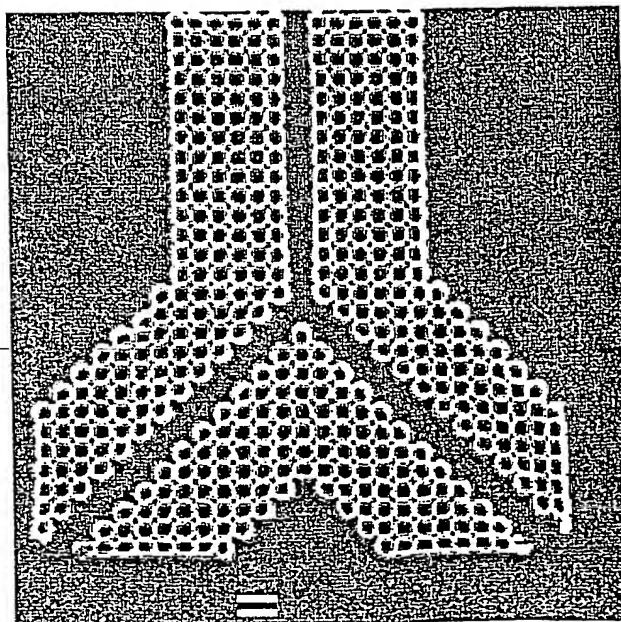
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*Figure 14**Figure 15*

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*Figure 16*



*Figure 17*

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/20264

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : H01J 37/30; B44C 1/22

US CL : 216/83, 87, 94, 101; 430/296

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
U.S. : 216/83, 87, 94, 101; 430/296

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
none

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EAST, STN (CAPLUS, INSPEC, JICST-EPLUS)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Rantala, J.T. et al. Electron radiation sensitive hybrid sol-gel materials for electron-beam lithography and diffractive optics. SPIE, July 1998, Vol. 3469, pages 30-37, especially page 33, lines 6+.	1-35
Y	Rantala, J.T. et al. Negative tone hybrid sol-gel material for electron-beam lithography. Thin Solid Films, 1999, Vol.345, pages 185-187, especially page 186, lines 10+.	1-35
Y	US 5,772,905 A (CHOU) 30 June 1998 (30.06.1998), column 4, lines 39-42.	12-22
Y	US 5,605,723 A (OGI et al) 25 February 1997 (25.02.1997), column 4, line 18; column 5, lines 42-62.	1-11
Y	US 5,271,797 A (KAMISAWA) 21 December 1993 (21.12.1993), column 5, lines 27-54.	1-11
A	JP 04-149090 A2 (ONODA CEMENT CO., LTD.) 22 May 1992 (22.05.1992), abstract.	1-35
A	JP 10-230560 A2 (DAINIPPON PRINTING CO., LTD) 02 September 1998 (02.09.1998), abstract.	1-35
A	JP 05-294863 A2 (DAINIPPON PRINTING CO., LTD.) 09 November 1993 (09.11.1993), abstract.	1-35

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Date of the actual completion of the international search

16 October 2001 (16.10.2001)

Date of mailing of the international search report

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